Comparison of 100 Micron Transmission Cell and the 3M© IR Card
for FT-IR Analysis of Military Fluids

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Abstract: The 100 micron transmission cell is the current method of choice for automated FT-IR analysis of lubricating and hydraulic oils. The transmission cell requires cleaning after each sample and thus use of a solvent. This paper outlines the preliminary results of a comparison between the 100 micron cell and the 3M© IR Card (microporous polyethylene substrate). Petroleum and polyol ester lubricating oils were used in the study. Statistical results and problems encountered are presented.

Key Words: Condition monitoring; Fourier transform infrared; FT-IR; polyethylene IR cards.

Introduction: The 100 micron transmission cell is the current method of choice for automated FT-IR analysis of lubricating and hydraulic oils [1]. The transmission cell requires cleaning after each sample and thus use of a solvent. This paper outlines the preliminary results of a comparison between the classic transmission cell and a solvent free approach for sample introduction—infrared (IR) Card. In this approach, the oil sample is applied to a microporous polyethylene substrate. The substrate simulates a 100 micron cell in that the same amount (thickness) of oil is absorbed into the substrate as would be in the 100 micron cell [2, 3, 4]. Use of an IR Card would eliminate the need for solvent; speed up the analysis time since no cell cleaning time or drying time is required; and virtually eliminate cross contamination since the Card is only used once. In addition, the simplicity of the Card lends itself well to minimal operator training, making the FT-IR even easier to operate. Sample analysis can be performed on as little as 20 microliters of sample.

Test and Evaluation: Used oil samples from ground and air equipment were analyzed concurrently by IR Card and 100 micron cell. The samples were analyzed on the same day to eliminate any change in laboratory conditions and further degradation of sample.
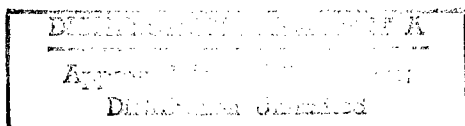
Settings on the FT-IR instrument were harmonized to obtain comparable results between the IR Card and cell e.g., the gain was lowered for the Card since the light beam does not have to penetrate two cell windows as with a 100 micron cell; the background reading is taken with an empty sample slot (no Card in place), etc. In contrast, the transmission cell may be in place for background readings. IR Card sample application and reproducibility are discussed in another paper [2].

Individual parameters in the various methods e.g. "petroleum", polyol ester", etc. were also harmonized to improve the comparison between the IR Card and cell e.g., the Card generates a slight baseline offset not seen with the transmission cell. Consequently, a minor modification of the soot analysis parameter (petroleum method) was required for the IR Card. The majority of the parameters in the petroleum and polyol ester methods remained unchanged.

For the most part, parameter readings were the same for both the cell and the Card, particularly for normal and marginal readings. For high parameter readings (high contamination or degradation), there tended to be a difference between the Card and the cell—the higher the reading, the greater the difference. The cell readings were almost always higher, suggesting a greater dynamic range. In this study, measurement linearity is quite reasonable within the current alarm limits.

Petroleum oil (Mil-L-2104): Oil samples from Army ground equipment and laboratory prepared samples were analyzed. This limited study included only 63 petroleum oil samples, insufficient for conclusive findings. However, the results are encouraging. The data is graphically presented in the figures below.
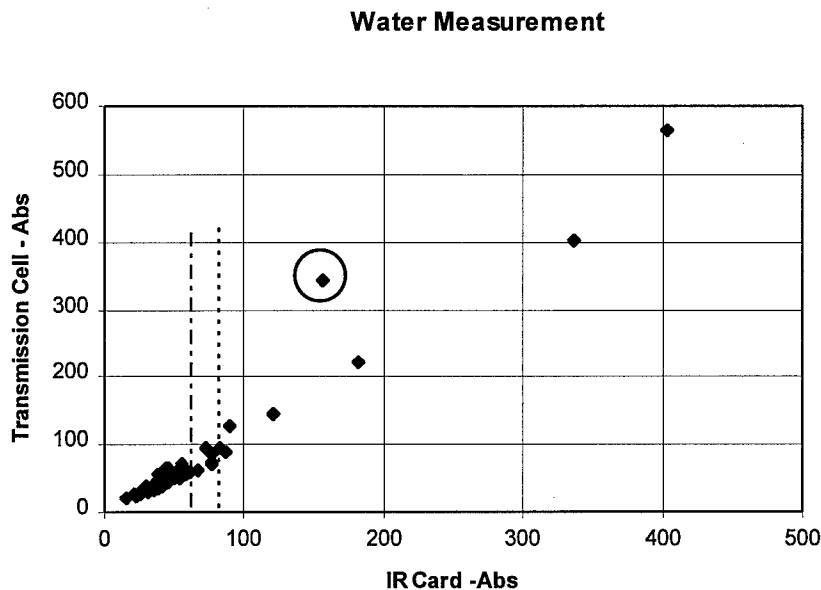
Water Measurement

Figure 1: Comparison of Water Data
Water measurement coefficient of correlation = 0.97

Water: Notice sample 633 (circled) where the values are 342 Absorbance (Abs) units (cell) and 156 Abs (Card). Reanalysis of the sample provided no explanation of the differences between the cell and the Card. Please note, this was a heavily contaminated sample. The left vertical dashed line indicates 2000 PPM (65 Abs) water and the right indicates 5000 PPM (80 Abs).
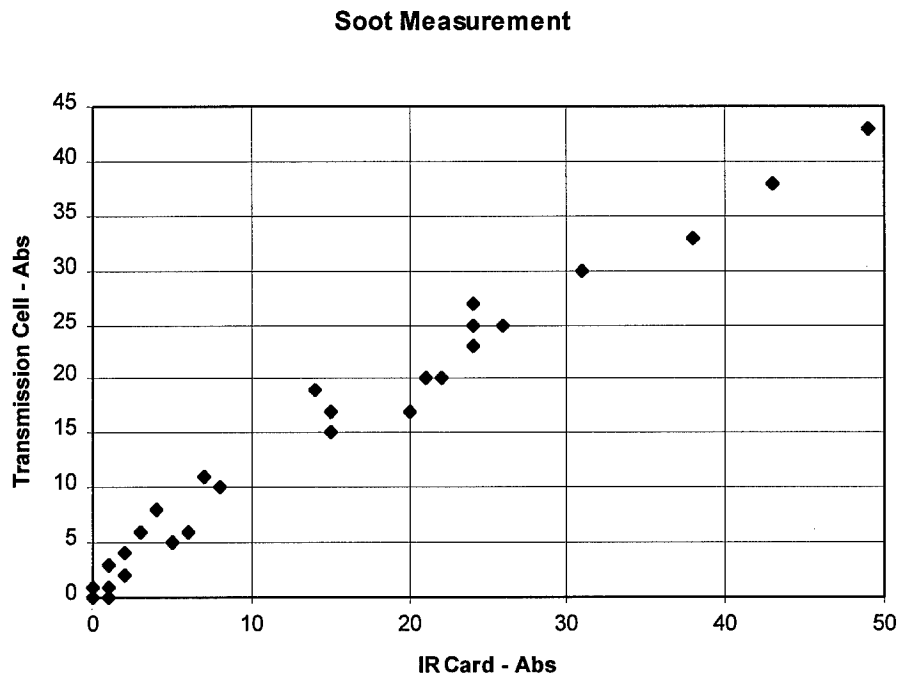
Soot Measurement

Figure 2: Comparison of Soot Data
Soot measurement coefficient of correlation = 0.99

Soot: Note, all samples were relatively free of soot. The current limit for heavy soot is 50 Abs.

Oil Degradation: Oil degradation by-products shown in Figures 3, 4 and 5 (oxidation, nitration and sulfation, respectively), have good correlation between the cell and the card. It should be noted that none of the samples were severely degraded. Current alarm limits are oxidation—18 Abs, nitration—14 Abs and sulfation—35 Abs.

Fuel: There were only a few samples with fuel contamination. Improvements in infrared detection for fuel contamination is ongoing for both the cell and the card.
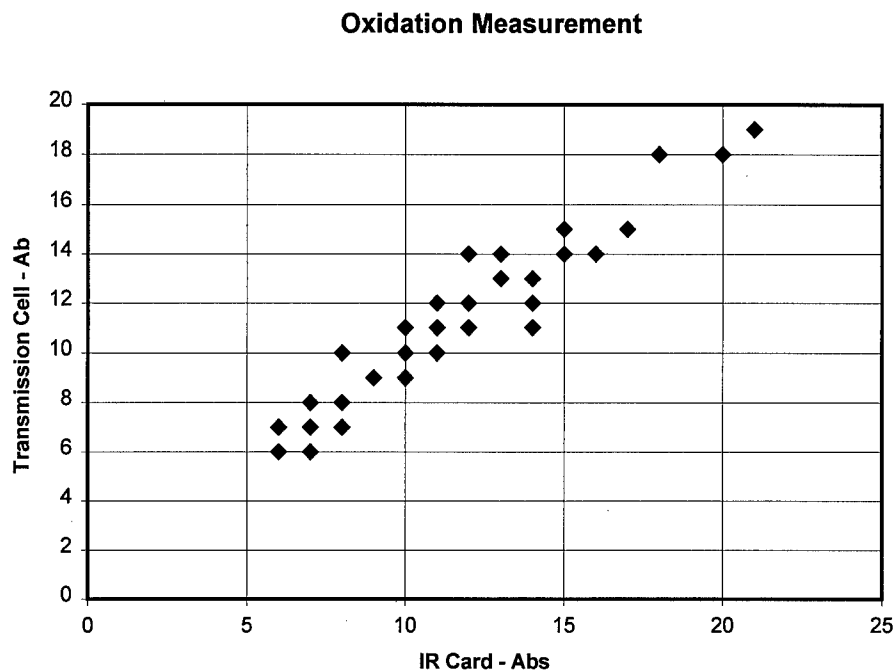
Oxidation Measurement

Figure 3: Comparison of Oxidation Data
Oxidation measurement coefficient of correlation = 0.97

Nitration Measurement
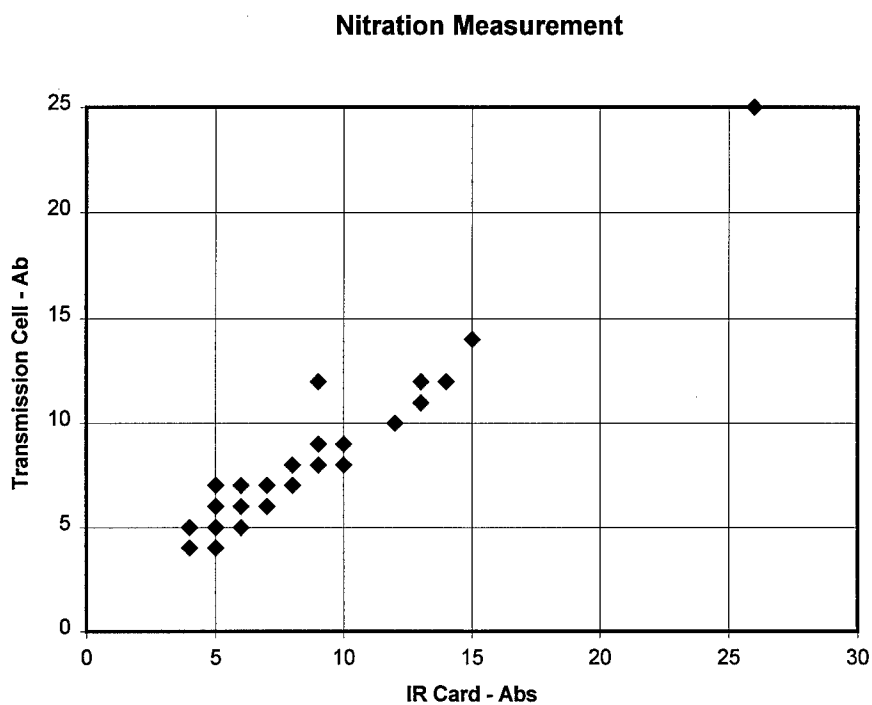
Figure 4: Comparison of Nitration Data
Nitration measurement coefficient of correlation = 0.97

Sulfation Measurement
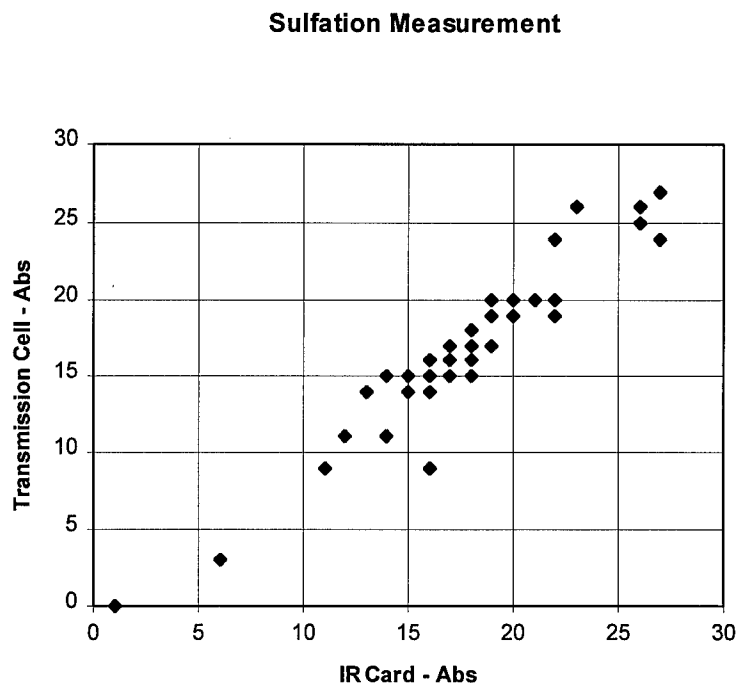
Figure 5: Comparison of Sulfation Data
Sulfation measurement coefficient of correlation = 0.95

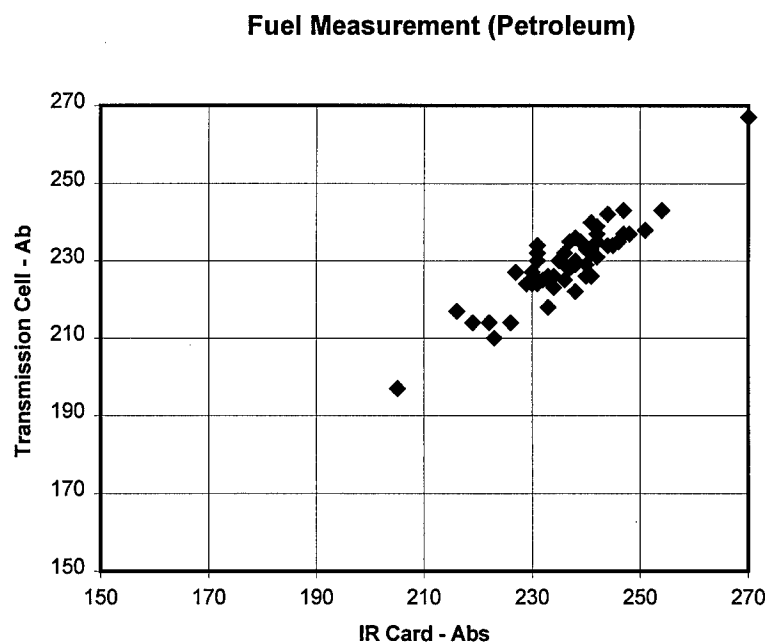**Fuel Measurement (Petroleum)**

Figure 6: Comparison of Fuel Data
Fuel measurement coefficient of correlation = 0.91
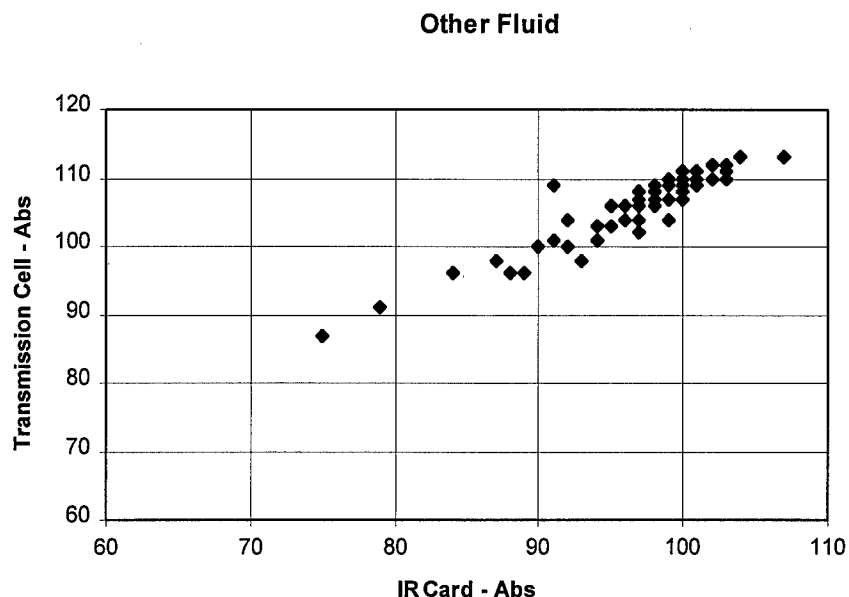
Other Fluid

Figure 7: Comparison of "Other Fluid" Data
"Other Fluid" measurement coefficient of correlation = 0.93

Other Fluid: "Other fluid" indicates contamination by an incorrect oil, fuel, etc.

Antiwear results were comparable for the IR card and the cell. There is not an established alarm limit for antiwear in petroleum oils. There were only a few samples with glycol contamination. On these samples, the results were comparable.

Polyol Esters (Mil-L-23699, Mil-L-7808): The study analyzed 190 oil samples from Army air and ground (M1A1) equipment, JOAP-TSC (laboratory prepared) and NAWCAD (laboratory degraded). In general, the IR Card showed a decrease in sensitivity below 1000 cm^{-1} which prevented meaningful readings for antiwear and "other fluid" contamination. To overcome the antiwear problem, a new region is being evaluated for polyol esters. In addition, water contamination in polyol esters cannot be measured using the IR Card. When a water contaminated sample is placed on the Card, the water immediately separates from the polyol ester and rolls to the outer edges of the substrate. Water contaminated Cards were examined microscopically and water droplets could be seen around the outer edges. A possible explanation for this phenomenon is that water is loosely bound to polyol esters (free hydroxyl and single bridge hydrogen bonding [5]) and the oil prefers the substrate to the water. Results are shown in the figures below.

Lubricant Breakdown: There is very good correlation between the cell and card for lubricant breakdown regions (I and II). No discrepancies were noted and there were numerous samples over the limits. (Limits shown are for approximately 1.0 mg KOH/ml and 1.5 mg KOH/ml.)
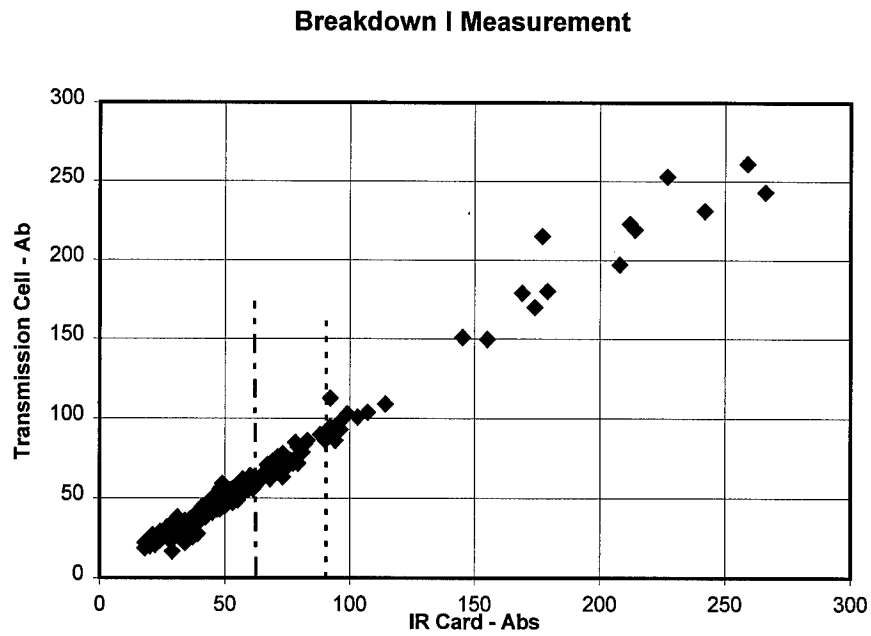
Breakdown I Measurement

Figure 8: Comparison of Lubricant Breakdown (region I) Data
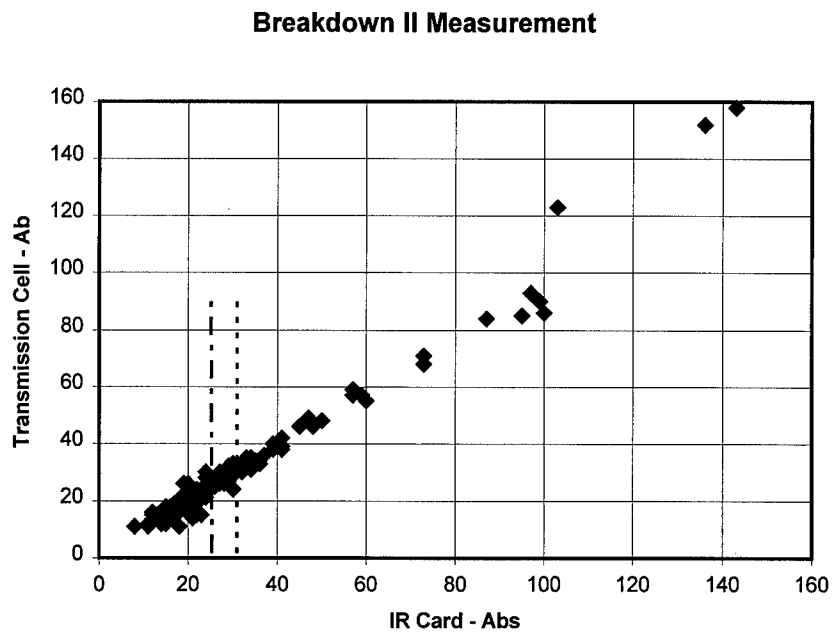Breakdown I measurement coefficient of correlation = 0.99

Breakdown II Measurement

Figure 9: Comparison of Lubricant Breakdown (region II) Data
Breakdown II measurement coefficient of correlation = 0.99
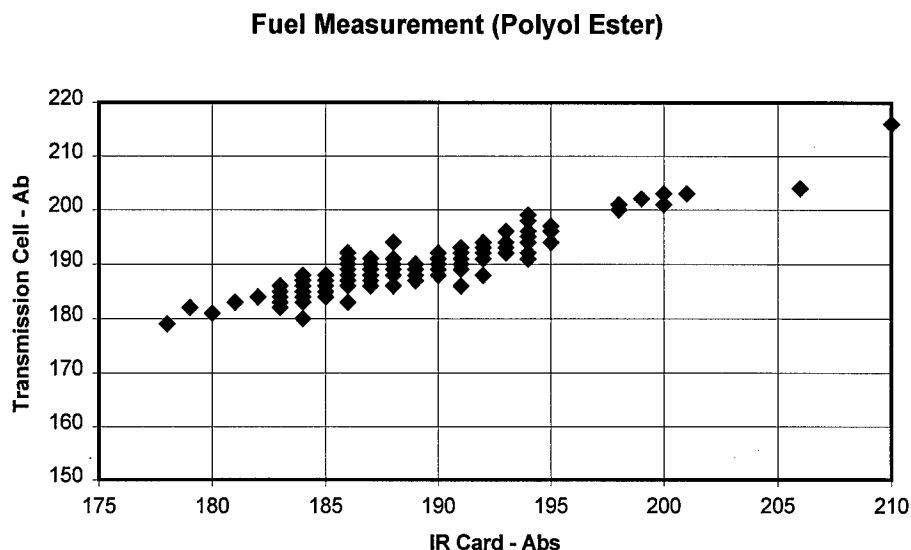
Fuel Measurement (Polyol Ester)

Figure 10: Comparison of Fuel Data
Fuel measurement coefficient of correlation = 0.93

Fuel: There were only a few samples with fuel contamination. Improvements in infrared detection for fuel contamination is ongoing for both the cell and the card.

Conclusions: This study included only 63 petroleum and 190 polyol ester oil samples and as such is insufficient for conclusive findings. However, the results are encouraging, especially for petroleum lubricants. The IR Card will eliminate solvent use, reduce analysis time, virtually eliminate cross contamination and simplify FT-IR operation.

The IR Card manufacturer is researching ways to resolve the polyol ester analysis problems (water and other fluid). In addition, the JOAP-TSC is evaluating a new antiwear measurement area for polyol ester oils.

References:

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